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Preparation and Structural Characterisation of Iron Oxide Nano-particles from Iron rust – a Novel Material and Eco-friendly method

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ABSTRACT

As efforts are underway to identify new sources and methods of preparation of iron oxide nanoparticles and their surface functionalisation, presently the ill-defined iron rust materials are transformed into viable alpha iron oxide (α Fe2O3) possessing characteristics features similar to that of α Fe2O3 synthesised thro various wet and dry methods. This paper explains a simple method of preparation of alpha iron oxide from rust particles by annealing at 700 C and characterisation of the processed nano-sized materials thro X-ray Diffraction matching with JCPDS standards , Electron Dispersive spectrum showing elemental composition as 60.62 % Fe and 39.38 % O and SEM analysis and crystalline domain size ranged between 110 - 581 nm. In the millennium of recycling and reuse of matter and energy, this paper would be catalytic in initiating a new line of research-converting waste into use.

Keywords: Iron nano particles – rust – characterisation-XRD-SEM-EDS-methodology.

INTRODUCTION

Nano-sized iron oxide particles have emerged as versatile materials for different applications. The structure-function relationship of these nano particles have been intensively studied because of the application in diverse fields, such as in catalysis, chemical sensors, rechargeable lithium-ion batteries, magnetic devices, electrode materials and pigments owing to its high resistance to corrosion, low processing cost and non toxicity[1]. Applications in magnetic storage, gas

sensing, biomedical, and catalysis applications[2,3,4&5], use in photo electro-chemical (PEC) water splitting reaction for the production of hydrogen[6,7,8,9,10,11&12]. The versatile nanoparticels are prepared from a variety of methods. The most common methods including co-precipitation, thermal decomposition, hydrothermal synthesis, micro emulsion and sonochemical synthetic route can all be directed to the synthesis of high quality of iron oxide nano particels. To mention few, reactive sputtering[13] pulsed laser evaporation[14] spray pyrolysis[15], sol gel processes[16]; hydrothermal technique[17,18] chemical vapour deposition[18] electro-chemical synthesis[19,20] hydrothermal approach, catalytic synthesis, flame spray pyrolysis, non aqueous synthesis, surfactant assisted method such as CTAB etc[21] laser pyrolysis techniques[22] microorganism or bacterial synthesis especially the Magneto-tactic bacteria and iron reducing bacteria[23,24] hydrolysis, thermolysis of precursors as well as co-precipitation technique[25] Obviously, in all methods available for synthesis of iron nanoparticles, a variety of chemicals reagents are used directly or indirectly. Unlike the existing synthetic methods, in the present study rust - a waste metallic substance is taken as the prime source of iron oxide nanoparticles preparation. Generally it is known that Rust is iron(III) oxide but shares several properties as rust consists of hydrated iron (III) oxides Fe2O3·nH2O and iron (III) oxide-hydroxide (FeO (OH), Fe (OH)3). It could also be stated that rust is an ill-defined material, described as hydrated ferric oxide[26] In the present study a methodology to prepare iron oxide nano-sized particles from iron rust has been evolved and the product prepared thro that method has been tested for its spectral characteristics. Further, it is learnt from literature survey that this may be the first attempt preparing nanosized particles from rust thro the methodology newly developed in the present study.

MATERIALS AND METHOD

Collection and pre-processing of rust

About 50 g. of rust is collected from the rusted iron rods and ironflats stocked in scrap yard in Pondicherry by gently rubbing the rusted surfaces with hard but short brushes. Further, it is crushed in a pestle mortar to make it powder as the rust collected from the scrap are granular and coarse. This powder is washed thrice in distilled water by filtering thro No.20 mesh net to remove adhering organic debris and other impurities. The washed rust powder is collected in petri dishes and dried in oven at 110C overnight. The oven dried powder is transferred to crucible and annealed at 700C for 1 hr in furnace. Once again, the annealed powder is crushed in pestle mortar to obtain ultrafine rust powder.

Processing and characterisation

To the annealed and cooled ultrafine rust powder, clear solution of 20% starch is slowly added by stirring. After adding starch, the content is heated to 70C for 15minites in a heating mantle. During heating, oxalic acid as surfactant, is added to the content drop by drop and stirring is required continuously. After 15 minutes of processing in oxalic acid, the mixture is filtered through No.20mesh net till the acidity due to oxalic acid is completely

removed. The filtrate is collected and transferred to petri dishes and dried in oven at 110C for 12 hrs. The dried powder is milled at rpm for 10 minutes .The milled powder is analysed for characteristics using SEM, EDS and XRD –Scanning Electron Microscope Make: Hitachi, Model: S-3400N for Morphology of iron oxide nanoparticles; Elemental analysis was investigated using EDS from JEOL, Japan.. The powder X-ray diffraction (XRD) patterns were taken on a Xray diffractometer (XRD; X'Pert Explorer, PANalytical diffractometer) equipped with Cu- K□1 radiation (□ =1.5406 nm) using a generator voltage of 45 kV and a current of 40 mA were applied for the determination. Thermal system (TGA-DSA) make Model Q600 SDT and Q20 DSC ; Plannary Monomill Make:Fritch Model: Pulveresette Planetary Monomill Make : Fristch Model : Pulverisette-7 (Monomill used for milling). The crystallilne domain size (particle size) of the prepared nanoparticles are calculated using Scherrer Equation

RESULT AND DISCUSSION

Synthesis of iron oxides in the nano range for various applications has been an active and challenging area of research during the last two decades.Like many other nanoparticles, those of iron oxides and ferrites are prepared either via wt chemical routes such as colloidal chemicals or sol-gel method or by dry processes such as vapour deposition techniques[27] or wet chemical methods which include precipitation at ambient/elevated temperatures, surfactant mediation, emulsion/micro-emulsion, electro-deposition[28] All these processes require careful choice of pH, concentration of the reactants, temperature, method of mixing, and rate of oxidation[29] and a variety of both organic and inorganic chemicals such as Ferric chloride, urea, ammonia solution, acridine orange, butyl carbitol acetate, ethyl acetate, monosodium phosphate, disodium phosphate are used.

In contrast to the available methods of syntheses(briefed in the introductory part) ,in the present study a new method has been evolved and unusual material has been selected as the main source of material ,i.e. Nano-sized Iron oxide (alpha F2O3) particles are prepared from iron rust. The ultrafine rust particles after treating with oxalic acid as surfactant, is heated directly to 700C**.** [30, 31, 32] have produced iron oxide nano particles at 700 C thro chemical processes. During this annealing period any of the phases of Iron oxide in the sample change from black to brown and chemically proceeds to hematite and the surfactants bind to the surface of the nanocrysals[33]However, there are reports stating that even below 700C, iron oxide particles are produced in the chemical synthesis methods. (Mirabbos Hojamberdiev *et al.* 2012) which is not found suitable for the preparation of iron oxide particles from rust.

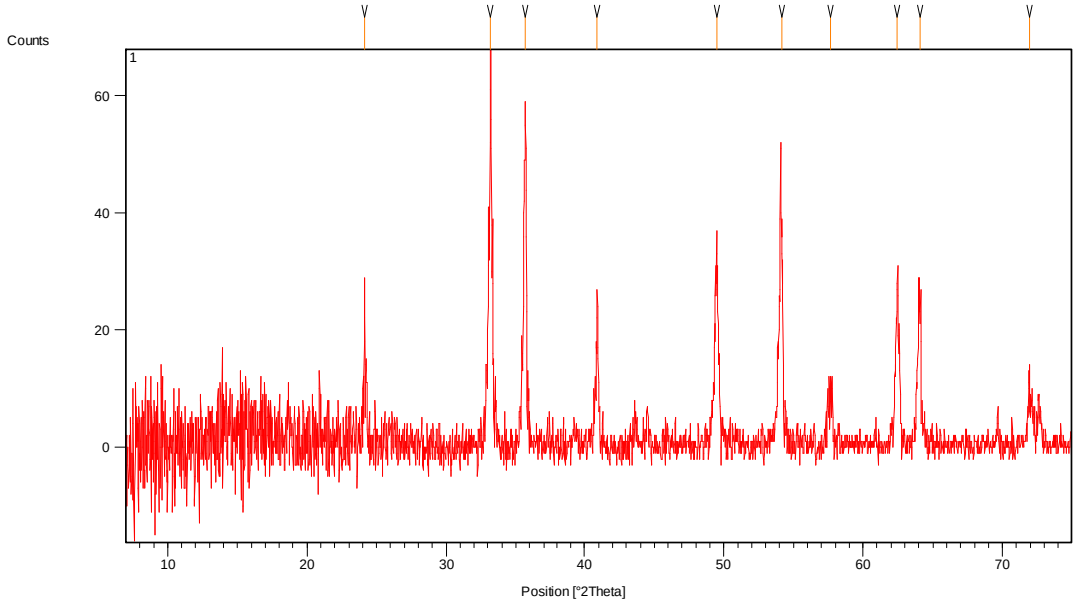
SPECTRAL CHARACTERISTICS

The X-ray diffractograms

XRD are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of metallic particles of varied size and shapes[26]. The sample showed the major characteristic peaks for prepared crystalline metallic iron at 2θ values of

24.16(012), 33.17(104), 35.17(110), 40.0(006), 49.50(024), 54.14(116), 57.64(018), 62.45(214), 64.07(300), 71.93(1110) degrees (Fig 1). All the reflection peaks in this pattern were found to match with the α -Fe2O3 phase having rhombohedral geometry (JCPDF # 79-1741) and well crystallined α -Fe2O3. These spectral data on XRD peaks are also similar to already reported spectra of chemically synthesized .alpha Iron Oxide[34,35].The crystalline domain size of the prepared nano particles are (particle size), calculated using Scherrer formula, ranged between 110nm and 581nm (Tab.1). It is realized that the assorted size range from 100nm might be due to the in adequate size and number of balls used in milling and timings. Work is in progress to achieve the alpha phase Iron oxide nanoparticels having almost all particles less than 100nm.

Fig. 1 XRD spectrum of α Fe2O3 nanoparticles (prepared from rust)showing characteristic peaks



Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
24.1600	21.00	0.2880	3.68076	30.88
33.1713	68.00	0.2400	2.69856	100.00
35.6833	55.00	0.1920	2.51414	80.88
40.9088	27.00	0.1920	2.20424	39.71
49.5000	27.00	0.2880	1.83992	39.71
54.1480	38.00	0.2400	1.69244	55.88
57.6454	11.00	0.4800	1.59780	16.18
62.4503	27.00	0.4320	1.48591	39.71
64.0781	24.00	0.2880	1.45203	35.29

71.9354	9.00	0.4800	1.31153	13.24

SEM images of iron oxide are presented in Fig. 2. It is clear from the SEM images that the particles prepared from rust are nano-sized formed in a very high-density exhibiting mostly spherical in shape but with aggregation which may be due to inadequate level of milling and /or overdose of surfactant. Further studies on these lines to obtain individual crystals, are underway.

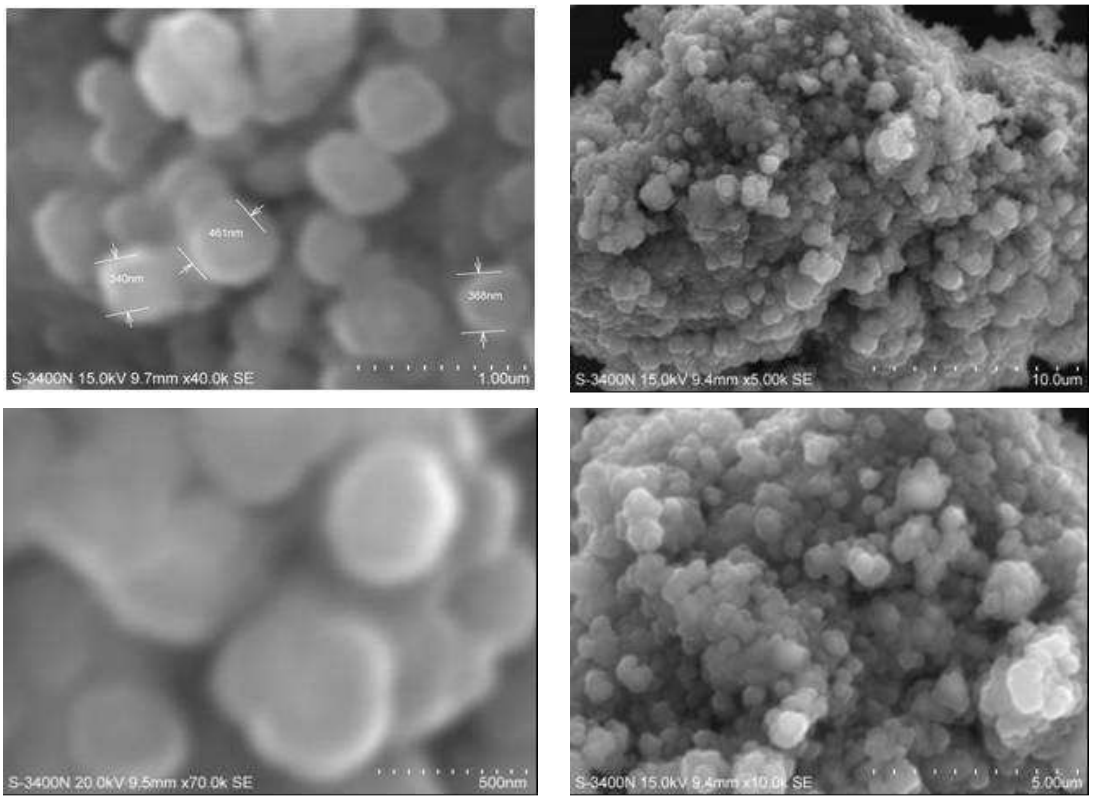


Fig.2 SEM images of Fe2O3 at different magnifications

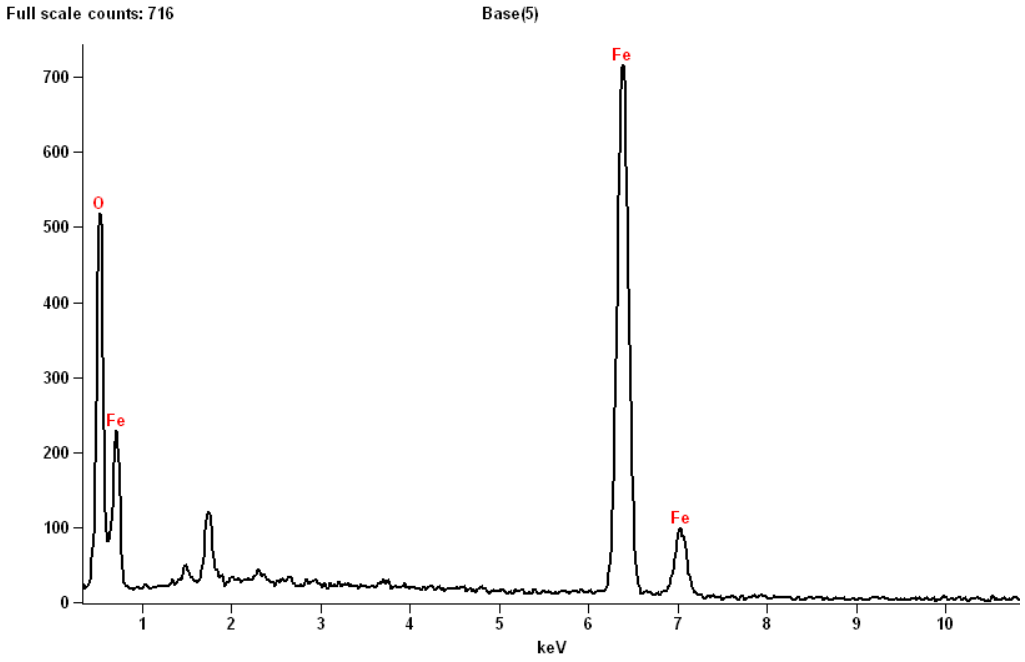
2θ of the intense peak(deg)	θ of the intense peak (deg)	FWHM of Intense peak (β)radians	Size of the particle (D)nm
24.16	12.08	0.000348	450.81
33.17	16.58	0.000371	581.13
35.68	17.84	0.001278	204.85
40.90	20.45	0.000697	143.39
49.50	24.75	0.000348	429.62
54.14	27.07	0.001011	382.55
57.64	28.82	0.000872	186.03
64.07	32.03	0.001395	110.41

71.93	35.96	0.000174	429.62

Table. 1 Crystalline domain size of the nanaopraticle obtained thro Scherrer equation

The electron dispersive spectroscopy (EDS) studies on these particles indicate the presence of only Fe and O composition and their composition is also very high i.e. Oxide and iron 39.38% and 60.63% (Fig. 3) respectively when compared previous report[26] where the composition is only 45.89% and 54.11% of Iron and oxide respectively. It is also obvious that even though these particles are prepared from rust- the ill defined metal oxide, it is not having any other elements or impurities achieved by the newly evolved methodology in this present study. Such characteristics are quite encouraging to make use of the rust as the source of eco-friendly material benefiting in two ways: recycling of rust powder and a potential alternative source for obtaining Iron oxide nanoparticels adopting simple method of preparation.

Fig.3 EDS spectrum showing characteristic elemental composition



Element Line	Net Counts	Net Counts Error	Weight %	Atom %	Formula
O K	3760	+/- 119	15.69	39.38	O
Fe K	12197	+/- 183	84.31	60.62	Fe
Fe L	2538	+/- 116	---	---	
Total			100.00	100.00	

Simultaneous TGA-DSC

From the TGA curve, (Fig. 4) it is understood that there is a gradual weight

loss during annealing upto to 700C and that loss is as attributed by[34] the weight loss above 200 ºC is due to the removal of loosely bound water of the sample and the dip between 400 and 700 ºC is attributed to the phase transformation from γ-Fe2O3 to α-Fe2O3. In the present study there is no such phased weight loss; instead there is a gradual weight loss to a maximum of only 2.5% which is very small when compared to previous reports [26,34] where the weight loss is observed to a maximum of 20% for the sample synthesised thro chemical process. On observing the DSC curves, it is clear that the sample exhibited only one exothermic peak at about 450^0C may indicating the transformation stage of ferromagnetic-paramagnetic.

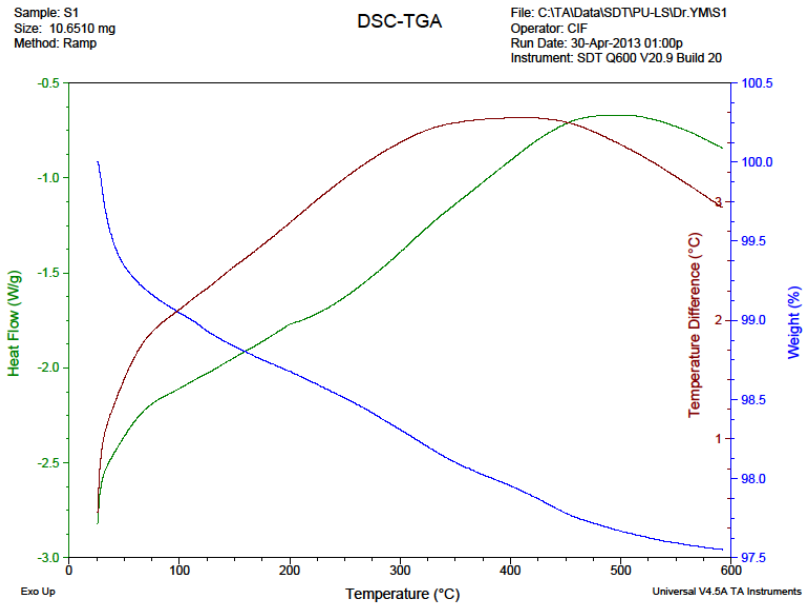


Fig.4 Simultaneous TGA-DSC spectrum exhibited by Fe2O3

Thus, it is very clear from the results obtained on the characteristics of nano-sized iron particles prepared from rust, that though iron rust is generally considered as an ill-defined metallic particles/powder, and found no place in the scope of material science, present study throws a bright light on the use of rust at par with the synthesised iron oxide nano-particles for its diversified applications in the near future. The new method developed in this study could also be further refined in such way that it would emerge as simple, scientific and environmentally benign methodology.

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